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A Novel CFC-12 Hydrolysis Catalyst: WO_3/SnO_2

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Abstract: The catalytic hydrolysis of dichlorodifluoromethane (CFC-12) was investigated over WO_3/SnO_2 solid acid which was prepared by impregnating $Sn(OH)_4$ with aqueous ammonium metatungstate followed by evaporating, drying and calcining in air. The CFC-12 conversion over WO_3/SnO_2 at 330°C remained above 99.5% during 150 h on stream, however, parent metal oxides showed rare catalytic decomposition activity.

Keywords: Environmental catalysis, Freon decomposition, WO_3/SnO_2 catalyst.

Thousands of studies have continuously confirmed that chlorofluorocarbons (CFCs) are killers of the stratospheric ozone which protects life on earth against harmful ultraviolet radiation from the sun[1]. Although many CFCs have been banned since the Montreal Protocol, there are still 2.25 million ton CFCs all over the world and numerous air-conditioning systems still use them. These CFCs are leaking out of existing equipments and will not be degraded in nature for 50-100 years because of their chemical inertness. Therefore, techniques that can eliminate CFCs either prior to or during their release to the environment are extremely desirable. Although CFCs can be destroyed by many techniques, catalytic hydrolysis seems to be the most promising one because of simple processes, requiring mild conditions and dioxines free. However, there are three major problems remaining to be tackled: (1) most of the catalysts decomposed CFCs completely at 350-550°C, which required a lot of energy and accelerated the deactivation rate; (2) measurable CFC-13 and even CO were reported to be found as by-products; (3) obvious deactivation was often found even during several hours on stream because HF and HCl produced during the reaction corroded the catalysts. In this paper, we will report a novel CFC-12 hydrolysis catalyst WO_3/SnO_2 which can minimize these three problems.

Amorphous $Sn(OH)_4$ was prepared by hydrolyzing $SnCl_4$ with ammonium hydroxide, washing, drying at 110°C and powdering. The hydroxide was impregnated with aqueous ammonium metatungstate followed by evaporating water, drying at 110°C, calcining in air at 600°C for 3h. The content of WO_3 was 0.2 g/gSnO_2 and the catalyst was labeled as WO_3/SnO_2. In comparison, pure WO_3 and SnO_2 samples were obtained by calcining ammonium metatungstate and $Sn(OH)_4$ at 600 °C for 3 h, respectively.

The catalytic hydrolysis of CFC-12 ($CCl_2F_2+2H_2O \rightarrow CO_2+2HF+2HCl$) was carried out using a conventional flow reaction apparatus. The reaction conditions were as follows: feed gas, CFC-12 1000 ppm, H_2O 6000 ppm, balance air; catalyst weight, 0.4 g; space velocity (WHSV), 6 l h^{-1} g-cat^{-1}. Effluent gases were passed through KOH solution continuously to remove HCl, HF and CO_2 produced during the reaction.

WO_3 and SnO_2 were both almost inactive for the CFC-12 hydrolysis at 330°C. Even at 500°C their activity was 62.7% and 98.1%, respectively. However, when WO_3 was supported on SnO_2, obvious enhancement in activity was found: WO_3/SnO_2 decomposed CFC-12 completely at 330°C and even at 300°C the conversion amounted to 85.2%. The acid amounts of the catalysts were examined by temperature programmed desorption of NH_3 (NH_3-TPD). For WO_3/SnO_2, sole large desorption peak appeared at 280°C and the total acid amount was 0.53 mmol/g, while the acid amounts of WO_3 and SnO_2 were only 0.22 and 0.29 mmol/g, respectively. This may explain the reason why WO_3/SnO_2 showed much higher activity than WO_3 and SnO_2. That is, acid centers play an important role on the catalytic decomposition of CFC-12, which is also recognized by many researchers[2-4]. In this study, a generation of acid sites by the combination of WO_3 and SnO_2 is clear, which was proved by the NH_3-TPD results and was well illuminated by the hypothesis of Tanabe *et al.*[5].

It was reported that CFC-13 and CO might be detected as by-products during the CFC-12 decomposition. Since they are both atmospheric pollutants, their formation is not desirable. In our results, no CO was found for all the catalysts and the selectivity to CFC-13 on WO_3/SnO_2 (0.42%) was much lower than that on pure SnO_2 (3.58%).

The catalytic life is another important factor for practical use. In our results, no deactivation was observed for WO_3/SnO_2 during 150 h on stream at 330°C and the selectivity to by-product CFC-13 ranged between 0.40% and 0.45%. There was no obvious difference between the XRD patterns of the fresh and used WO_3/SnO_2. Perhaps it is tungsten oxide species which covered the SnO_2 surface that gave HF less opportunity to attack the SnO_2 surface thus suppressed the deactivation. Similar protective effect was also reported for the transition metal chloride modified γ-Al_2O_3[4].

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